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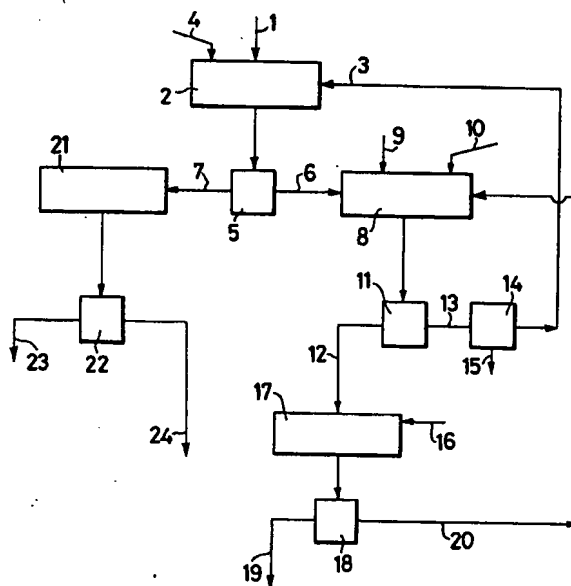
(54) Metal recovery

(57) There is disclosed a process for recovering metals of high commercial value from a sludge (1) containing lead, antimony, silver, arsenic, bismuth and copper, by a wet method, by treating (2) the sludge (1) with aqueous hydrochloric acid (3) accompanied by air injection (4). The treated sludge is separated (5) into a silver-enriched fraction (6) and a silver-depleted solution (7). The fraction (6) is treated

(8) with aqueous hydrochloric acid (9) and the treated fraction is separated (11) into an argentiferous residue (12) from which silver is recovered and a solution (13) enriched in hydrochloric acid and lead chloride.

The solution (7) is cooled (21) and filtered (22) to obtain a residue (23) enriched in lead chloride from which lead may be recovered and a solution (24) containing chlorides of antimony, bismuth, silver, arsenic, copper and lead from which these elements may be recovered.

Fig.1



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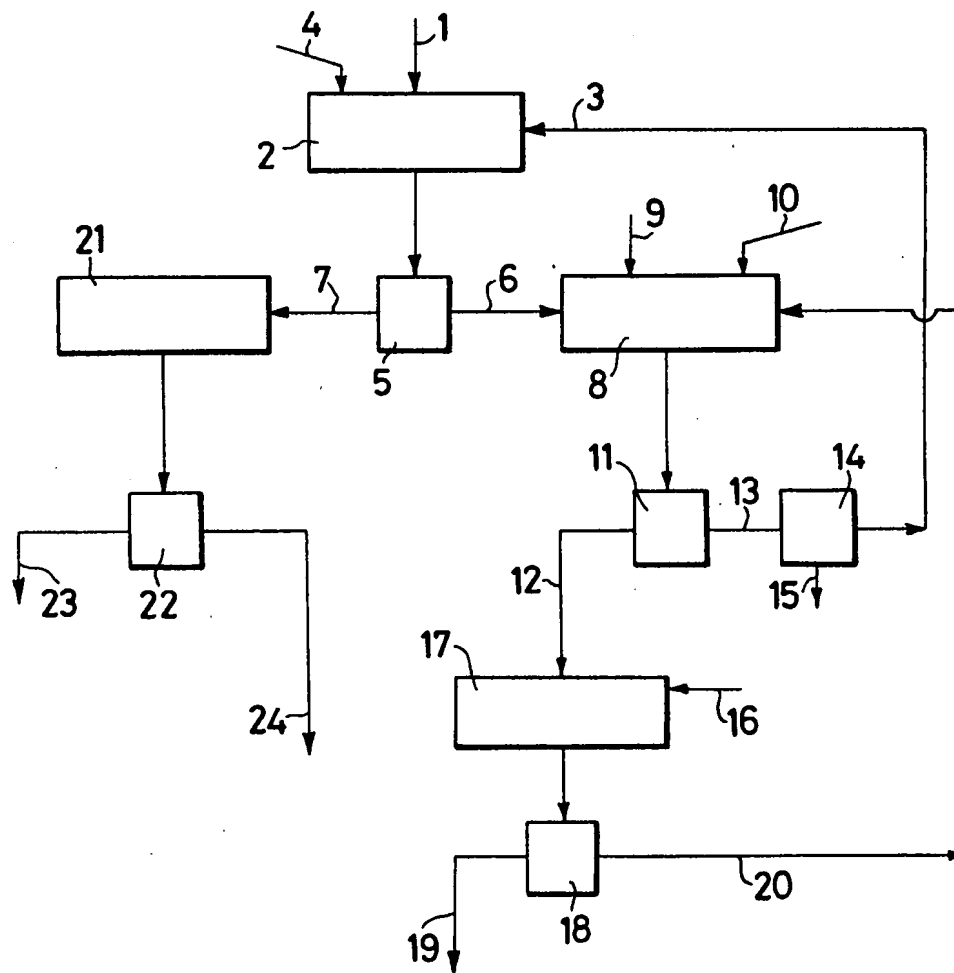
Fig.1

Fig.2

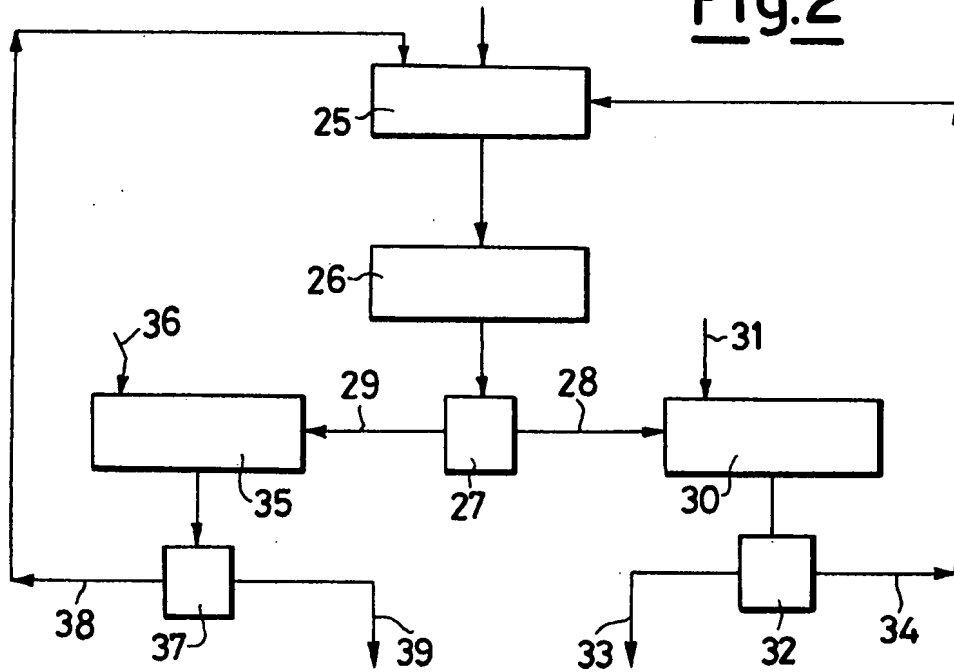
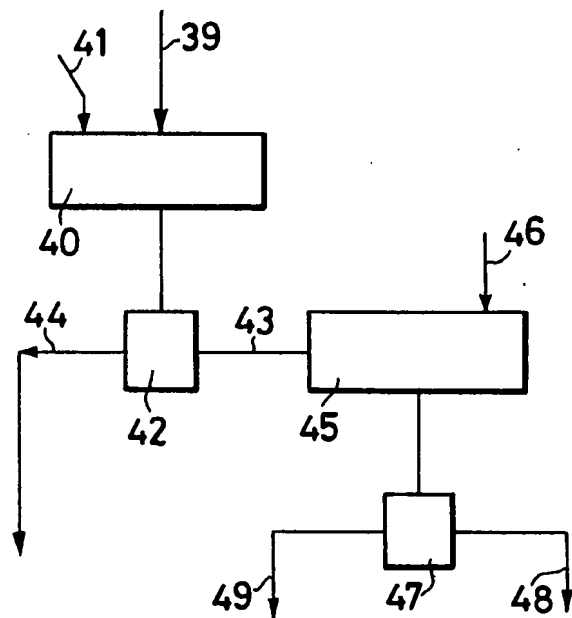


Fig.3



SPECIFICATION

Metal recovery

- 5 This invention relates to a process for recovering metals of high commercial value from a material containing such metals such as a mud or sludge containing lead, antimony and possibly other metals.
- 10 Such a sludge is treated in known processes by a dried method. The operations involved in this dry method are very complicated, and lead to both economical and ecological problems.
- It has now been surprisingly found that the
- 15 drawbacks of the known art can be overcome by a process mainly involving a wet route. This process has substantially economical advantages, giving higher yields with lower costs, together with substantial ecological advantages as it no longer produces fumes.
- 20 The process according to the present invention for recovering metals of high commercial value from a sludge containing lead and/or antimony, and possibly other metals, including silver and/or arsenic and/or bismuth and/or copper, each in elemental
- 25 and/or combined form, comprises treating the sludge at least once by a wet method with hydrochloric acid in aqueous solution, optionally accompanied by air injection.
- 30 More particularly, where the sludge, besides containing lead and antimony, also contains silver, arsenic, bismuth and copper in such quantities as to make their recovery also convenient, the process preferably comprises the following steps:
- 35 (a) treating the sludge with aqueous hydrochloric acid accompanied by air or oxygen injection;
- (b) decanting, syphoning and optionally filtering the treated sludge of step (a) to separate a thickened fraction enriched in silver from a solution depleted
- 40 thereof;
- (c) treating the thickened fraction of step (b) with aqueous hydrochloric acid, possibly accompanied by air or oxygen injection;
- (d) decanting, syphoning and optionally filtering
- 45 the treated thickened fraction of step (c) to separate an argentiferous residue from an aqueous solution rich in hydrochloric acid and lead chloride;
- (e) washing and filtering the argentiferous residue of step (d) to separate a purified
- 50 argentiferous residue enriched in silver chloride from an aqueous solution, which latter is recycled to step (c);
- (f) cooling and filtering the solution of step (b) to separate a residue enriched in lead chloride from a
- 55 solution containing antimony, bismuth, silver, arsenic, copper and lead chlorides;
- (g) cooling and filtering the aqueous solution enriched in hydrochloric acid and lead chloride of step (d) to separate a residue enriched in lead
- 60 chloride from a solution enriched in hydrochloric acid, which latter is recycled to step (a).
- The purified argentiferous residue withdrawn

from step (e) can subsequently be converted to silver by reacting it with zinc dust, ammonium hydroxide and water, or alternatively by direct reduction.

The lead chloride residues withdrawn from steps (f) and (g) can be subjected to lead recovery as a pure salt, or alternatively, if the sludge emanates from industrial lead electrorefining, they can be fed to the main lead treatment cycle.

The process of the present invention preferably includes the selective separation of the elements present in the solution containing antimony, bismuth, silver, arsenic, copper and lead chlorides formed in step (f) by the following steps:

- (i) hydrolysing the solution;
- (ii) cooling and filtering the hydrolysed solution to separate a residue containing antimony from a
- 80 solution depleted of antimony;
- (iii) washing the antimony-containing residue with aqueous hydrochloric acid and then filtering it to separate a residue containing antimony oxychloride from an aqueous solution, which latter is recycled to
- 85 step (i);
- (iv) neutralising the depleted solution of step (ii) with Na_2CO_3 or another neutralising agent and then filtering it to separate a residue, which is recycled to step (i), from an antimony-depleted solution containing bismuth, arsenic, silver, copper, lead and anti-
- 90 mony chlorides.

The process of the present invention preferably includes treating the antimony-depleted solution containing bismuth, arsenic, silver copper, lead and antimony chlorides formed in step (iv) by the

95 following steps.

- (v) neutralising the solution with Na_2CO_3 or another neutralising agent and then filtering it to separate a residue containing bismuth from a bismuth-depleted solution which is enriched in copper and arsenic chlorides;
- (vi) washing the bismuth-containing residue with
- 100 hydrochloric acid and then filtering it to separate a residue comprising bismuth oxychloride from an aqueous solution, which latter is recycled to the hydrolysis step (i).

The sludge is preferably treated in step (a) at a temperature of from 50° to 80°C and for a time of from 0.5 to 3.0 hours, while the thickened fraction is preferably treated in step (c) at a temperature again

110 of from 50° to 80°C but for a time of from 0.5 to 2.0 hours.

The molar concentration of the aqueous hydrochloric acid is preferably from 3 to 8M in step (a), and preferably from 4 to 8M in step (c).

In step (f) and step (g), both the silver-depleted solution and the solution enriched in hydrochloric acid and lead chloride are preferably cooled to a temperature of from 15° to 25°C .

120 The solution containing antimony, bismuth, silver, arsenic, copper and lead chlorides is hydrolysed in step (i) at a preferred temperature of from 65° to 75°C , and the hydrolysed solution is preferably cooled to a temperature of from 15° to 25°C .

The drawing(s) originally filed were informal and the print here reproduced is taken from a later filed formal copy.

Neutralisation with Na_2CO_3 is preferably carried out in the case of the antimony-depleted solution of step (iv) to give a final pH of from 1.2 to 2, and in the case of the solution of step (v) to give a final pH of from 2.0 to 2.8.

The molar concentration of the aqueous hydrochloric acid used in step (iii) to wash the antimony-containing residue is preferably from 0.5 to 0.7 M so as to attain a final pH of from 1 to 1.2, and that of the aqueous hydrochloric acid used in step (vi) to wash the bismuth-containing residue is preferably from 0.01 to 0.1 M so as to attain a final pH of from 2.2 to 2.5.

The invention will now be described, by way of example, with reference to the flow diagrams shown in Figures 1, 2 and 3 of the drawings.

Referring to Figure 1, a sludge 1, either in the wet state or precalcined in order to eliminate organic residues, is treated at point 2 with aqueous hydrochloric acid 3, accompanied by air or oxygen injection 4.

The treated sludge is subjected to decantation, syphoning and possibly hot filtration at point 5, by means of which a silver-enriched thickened fraction 6 is separated from a silver-depleted solution 7. The silver-enriched thickened fraction 6 is subjected to a second treatment at point 8 with aqueous hydrochloric acid 9, possible accompanied by air or oxygen injection 10. The treated thickened fraction is itself subjected to decantation, syphoning and possibly hot filtration at point 11, in order to separate an argentiferous residue 12 from an aqueous solution 13 enriched in hydrochloric acid and lead chloride.

The aqueous solution 13 is cooled and filtered at point 14 in order to separate a residue 15 enriched in lead chloride from an aqueous solution 3 enriched in hydrochloric acid, which is recycled to point 2. The argentiferous residue 12 is washed with water 16 at point 17, and subsequently filtered at point 18 to separate a purified argentiferous residue 19 from an aqueous solution 20 which is recycled to point 8.

The silver-depleted solution 7 is cooled at point 21 and subsequently filtered at point 22 to separate a residue 23 enriched in lead chloride from a solution 24 containing antimony, bismuth, silver, arsenic, copper and lead chlorides.

If the sludge emanates from industrial lead electrefining, the residues 15 and 23 enriched in lead chloride can be fed to the main lead treatment cycle, or alternatively the lead can be recovered as the pure salt.

The subsequent selective separation of the elements from solution 24 is shown diagrammatically in Figures 2 and 3.

The solution 24 containing antimony, bismuth, silver, arsenic, copper and lead chlorides is subjected to hydrolysis at point 25, cooled at point 26 and then filtered at point 27 to thus separate a residue 28 containing a high percentage of antimony from an antimony-depleted solution 29. The residue 28 is washed at point 30 with aqueous hydrochloric acid 31, and filtered at point 32 to thus separate a residue 33, containing mainly antimony oxychloride, from an aqueous solution 34 which is recycled to point 25.

The antimony-depleted solution 29 is neutralised at point 35 with Na_2CO_3 or another neutralising agent 36, and filtered at point 37 to separate a residue 38, which is recycled to point 25, from a solution 39 containing bismuth, arsenic, silver, copper, lead and antimony chlorides, in which the bismuth, arsenic and possibly the copper are present in high amounts.

The antimony-depleted solution 39 is neutralised at point 40 with Na_2CO_3 or another neutralising agent 41, and filtered at point 42 to separate a residue 43 containing bismuth from a bismuth-depleted solution 44 which is rich in copper and arsenic chlorides.

The bismuth-containing residue 43 is washed at point 45 with hydrochloric acid in aqueous solution 46, and filtered at point 47 to separate a residue 48 containing mainly bismuth oxychloride, from an aqueous solution 49 which is recycled to point 25.

The invention will now be illustrated by the following Example in which reference is made to the Figures.

EXAMPLE

The feed used was an anodic sludge emanating from lead electrefining, having a weight in the wet state (w.w.) of 10000 g, a solids content (s.w.) of 7936 g, and the following composition;

Sb	41.34% (3280.7g)
Bi	8.64% (685.7g)
Ag	7.86% (623.7g)
As	6.18% (490.4g)
Cu	2.49% (197.6g)
Pb	8.10% (642.8g)

74.61% (5920.9g).

The remainder of the solids content to 100% (i.e. 25.39%) consisted of combined oxygen, combined sulphur, halogens, silica and organic material.

The first treatment with hydrochloric acid was carried out at 60°C for 3 hours with 6M aqueous hydrochloric acid, accompanied by air injection. The second treatment with hydrochloric acid was carried out again at 60°C but for 2 hours with 7.5M aqueous hydrochloric acid.

The washed argentiferous residue 19, having a w.w. of 1793 g and a s.w. of 1201 g, consisted of:

Sb	0.19% (2.3g)
Bi	0.042% (0.5g)
Ag	48.61% (583.8g)
As	0.035% (0.4g)
Cu	0.012% (0.1g)
Pb	13.25% (159.1g)

The remainder of the solids content to 100% consisted of combined oxygen, combined sulphur, halogens, silica and organic material.

The residue 23, containing essentially lead chloride and having a w.w. of 721 g and a s.w. of 582.2g, consisted of:

Sb	1.43% (8.3g)
Bi	0.31% (1.8g)
Ag	5.41% (31.5g)
As	0.24% (1.4g)
Cu	0.096% (0.6g)
Pb	63.07% (367.2g)

The chloride solution 24, to be fed to the stage for

separating the metals contained in it and having a volume of 43.400 litres, consisted of:

	Sb	75.35 g/litre (3270.2g)
	Bi	15.79 g/litre (685.3g)
5	Ag	0.20 g/litre (8.7g)
	As	11.26 g/litre (488.7g)
	Cu	4.54 g/litre (197.0g)
	Pb	2.69 g/litre (116.7g).

The hydrolysis was carried out at a temperature of 70°C, followed by cooling to 20°C.

The neutralisation at point 35 was carried out to a final pH of 1.7, whereas the washing at point 30 resulted in a final pH of 1.

The residue 33, having a w.w. of 7578.7g and a s.w. of 4300.6 g, consisted of:

	Sb	66.62% (2865.0g)
	Bi	0.25% (10.7g)
	Ag	0.092% (3.9g)
	As	2.30% (98.9g)
20	Cu	0.02% (0.8g)
	Pb	0.28% (12.0g).

The antimony-depleted solution 39, having a volume of 235.59 litres, consisted of:

	Sb	0.46 g/litre (108.4g)
25	Bi	2.21 g/litre (520.6g)
	Ag	0.0081g/litre (1.9g)
	As	1.35 g/litre (318.0g)
	Cu	0.82 g/litre (193.2g)
	Pb	0.26 g/litre (61.2g).

The sludge residue 38, which was recycled to the hydrolysis stage and had a w.w. of 3179.6g and a s.w. of 1012.47 g, consisted of;

	Sb	29.39% (297.5g)
	Bi	15.13% (153.2g)
35	Ag	0.277% (2.8g)
	As	7.05% (71.4g)
	Cu	0.22% (2.2g)
	Pb	4.27% (43.2g).

The antimony-depleted solution 39 was neutralised at point 40 to a final pH of 2.3. The subsequent wash 44 was carried out to a final pH of 2.3.

The residue 48, having a w.w. of 2269 g and a s.w. of 926 g, consisted of:

	Sb	6.82% (63.1g)
45	Bi	55.89% (517.5g)
	Ag	0.063% (0.6g)
	As	1.05% (9.7g)
	Cu	0.097% (0.9g)
	Pb	6.27% (58.1g).

The bismuth-depleted solution 44 having a volume of 228.506 litres, consisted of:

	Sb	0.193 g/litre (44.1g)
	Bi	0.0175 g/litre (4.0g)
	Ag	0.0057 g/litre (1.3g)
55	As	1.35 g/litre (308.5g)
	Cu	0.84 g/litre (192.0g)
	Pb	0.015 g/litre (3.4g).

CLAIMS

1. A process for recovering metal from a sludge containing lead and antimony, which comprises treating the sludge at least once by a wet method with aqueous hydrochloric acid optionally accompanied by air or oxygen injection.

2. A process as claimed in claim 1, wherein the sludge contains silver, arsenic, bismuth, copper,

lead and antimony, in elemental and/or combined form.

3. A process as claimed in claim 2, wherein the sludge is subjected to the following steps:

(a) treating the sludge with aqueous hydrochloric acid optionally accompanied by air or oxygen injection;

(b) separating (for example by decanting, syphoning and optionally filtering) the treated sludge of step (a) into a thickened fraction enriched in silver and a solution depleted thereof;

(c) treating the thickened fraction of step (b) with aqueous hydrochloric acid optionally accompanied by air or oxygen injection;

(d) separating (for example by decanting, syphoning and optionally filtering) the treated thickened fraction of step (c) into an argentiferous residue and an aqueous solution enriched in hydrochloric acid and lead chloride;

(e) washing and filtering the argentiferous residue of step (d) to separate a purified argentiferous residue enriched in silver chloride from an aqueous solution, which latter is recycled to step (c);

(f) cooling and filtering the solution of step (b) to separate a residue enriched in lead chloride from a solution containing antimony, bismuth, silver, arsenic, copper and lead chlorides; and

(g) cooling and filtering the aqueous solution enriched in hydrochloric acid and lead chloride of step (d) to separate a residue enriched in lead chloride from a solution enriched in hydrochloric acid, which latter is recycled to step (a).

4. A process as claimed in claim 3, wherein the purified argentiferous residue of step (e) enriched in silver chloride is converted to silver by reacting it with zinc dust, ammonium hydroxide and water.

5. A process as claimed in claim 3, wherein the purified argentiferous residue of step (e) enriched in silver chloride is converted to silver by direct reduction.

6. A process as claimed in any of claims 3 to 5, wherein the residues enriched in lead chloride of steps (f) and (g) are fed to a main lead treatment cycle.

7. A process as claimed in any of claims 3 to 5, wherein the residues enriched in lead chloride of steps (f) and (g) are subjected to recovery of lead in the form of a pure salt.

8. A process as claimed in any of claims 3 to 7, wherein the sludge is treated in step (a) at a temperature of from 50° to 80°C for a period of from 0.5 to 3.0 hours.

9. A process as claimed in any of claims 3 to 8, wherein the thickened fraction is treated in step (c) at a temperature of from 50° to 80°C for a period of from 0.5 to 2 hours.

10. A process as claimed in any of claims 3 to 9, wherein the silver-depleted solution is cooled in step (f) to a temperature of from 15 to 25°C.

11. A process as claimed in any of claims 3 to 10, wherein the solution enriched in hydrochloric acid and lead chloride is cooled in step (g) to a temperature of from 15 to 25°C.

12. A process as claimed in any of claims 3 to 11, wherein the molar concentration of the aqueous

hydrochloric acid used in step (a) is from 3 to 8 M.

13. A process as claimed in any of claims 3 to 12, wherein the molar concentration of the aqueous hydrochloric acid used in step (c) is from 4 to 8 M.

5 14. A process as claimed in any of claims 3 to 13, wherein the solution containing antimony, bismuth, silver, arsenic, copper and lead chlorides of step (f) is subjected to the following steps:

(i) hydrolysing the solution;

10 (ii) colling and filtering the hydrolysed solution to separate a residue containing antimony from a solution depleted of antimony;

(iii) washing the antimony-containing residue with aqueous hydrochloric acid and then filtering it to

15 separate a residue containing antimony oxychloride from an aqueous solution, which latter is recycled to step (i); and

(iv) neutralising the depleted solution of step (ii) with Na_2CO_3 or another neutralising agent and then

20 filtering it to separate a residue, which is recycled to step (i), from an antimony-depleted solution containing bismuth, arsenic, silver, copper, lead and antimony chlorides.

25 15. A process as claimed in claim 14, wherein the solution containing antimony, bismuth, silver, arsenic, copper and lead chlorides is hydrolysed in step (i) at a temperature of from 65 to 75°C.

30 16. A process as claimed in claim 14 or 15, wherein the hydrolysed solution is cooled in step (ii) to a temperature of from 15 to 25°C.

17. A process as claimed in any of claims 14 to 16, wherein the antimony-depleted solution is neutralised in step (iv) with Na_2CO_3 to a final pH of from 1.2 to 2.

35 18. A process as claimed in any of claims 14 to 17, wherein the molar concentration of the aqueous hydrochloric acid used in step (iii) for washing the antimony-containing residue is from 0.5 to 0.7 M in order to attain a final pH of from 1 to 1.2.

40 19. A process as claimed in any of claims 14 to 18, wherein the antimony-depleted solution containing bismuth, arsenic, silver, copper, lead and antimony chlorides of step (iv) is subjected to the following steps:

45 (v) neutralising the solution with Na_2CO_3 or another neutralising agent and then filtering it to separate a residue containing bismuth from a bismuth-depleted solution which is enriched in copper and arsenic chlorides; and

50 (vi) washing the bismuth-containing residue with hydrochloric acid and then filtering it to separate a residue comprising bismuth oxychloride from an aqueous solution, which latter is recycled to step (i).

55 20. A process as claimed in claim 19, wherein the solution is neutralised in step (v) with Na_2CO_3 to a final pH of from 2.0 to 2.8.

21. A process as claimed in claim 19 or 20, wherein the molar concentration of the aqueous hydrochloric acid used in step (vi) for washing the bismuth-containing residue is from 0.01 to 0.1 in order to attain a final pH of from 2.2 to 2.5.

22. A process as claimed in claim 1, substantially as hereinbefore described with reference to Figures 1, 2 and 3 of the drawings.

65 23. A process as claimed in claim 1, substantially

as described in the foregoing Example.

24. A metal recovered by a process as claimed in any of claims 1 to 23.

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